|              |               | 430  | <u>orec'd PCT/PTO 27 Jan 2000</u>  |  |  |  |  |  |
|--------------|---------------|--|--|--|--|--|--|--|
| FORM<br>(REV |               | 90 (Modified)  U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE   | ATTORNEY'S DOCKET NUMBER   |  |  |  |  |  |
|              | TI            | RANSMITTAL LETTER TO THE UNITED STATES   | MAT-7886US   |  |  |  |  |  |
|              |               | DESIGNATED/ELECTED OFFICE (DO/EO/US)   | U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR                               |  |  |  |  |  |
| i            | $\ell_{i_0}$  | CONCERNING A FILING UNDER 35 U.S.C. 371  | U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR<br>To Be Assigned 4 6 3 5 6 5 |  |  |  |  |  |
| INTE         |               | TIONAL APPLICATION NO. INTERNATIONAL FILING DATE   | PRIORITY DATE CLAIMED  |  |  |  |  |  |
| TITI         |               | PCT/JP99/02828 27 May 1999 (27/.05.99)  NVENTION   | 28 May 1998 (28.05.98)   |  |  |  |  |  |
| BAT          | TTER          | RY PLATE AND BATTERY   |  |  |  |  |  |  |
|              |               | T(S) FOR DO/EO/US<br>Hashimoto; Hiroyuki Murai; Yorihito Ohana; Hiroshi Matsuno; Hi  | ideya Asano  |  |  |  |  |  |
| Appl         | icant l       | herewith submits to the United States Designated/Elected Office (DO/EO/US) t   | he following items and other information:                                |  |  |  |  |  |
| 1.           | $\boxtimes$   | This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371   |  |  |  |  |  |  |
| 2.           | D/            | This is a SECOND or SUBSEQUENT submission of items concerning a filing   |  |  |  |  |  |  |
| 3.           | $(\boxtimes)$ |  |  |  |  |  |  |  |
|              |               | This is an express request to begin national examination procedures (35 U.S.C examination until the expiration of the applicable time limit set in 35 U.S.C. | 371(b) and PCT Articles 22 and 39(1).                                    |  |  |  |  |  |
| 4.           |               | A proper Demand for International Preliminary Examination was made by the  | e 19th month from the earliest claimed priority date.                    |  |  |  |  |  |
| 5.           | $\boxtimes$   | A copy of the International Application as filed (35 U.S.C. 371 (c) (2))   |  |  |  |  |  |  |
|              |               | a. \( is transmitted herewith (required only if not transmitted by the Inter   | rnational Bureau).   |  |  |  |  |  |
| 727          |               | b.  has been transmitted by the International Bureau.  |  |  |  |  |  |  |
|              |               | c. $\square$ is not required, as the application was filed in the United States Receiving Office (RO/US).  |  |  |  |  |  |  |
| <b>=</b> 6.  | $\boxtimes$   | A translation of the International Application into English (35 U.S.C. 371(c)(2)).   |  |  |  |  |  |  |
| _7.          | $\boxtimes$   | A copy of the International Search Report (PCT/ISA/210).   |  |  |  |  |  |  |
| լլ8.         | $\boxtimes$   | Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))  |  |  |  |  |  |  |
| H            |               | a. $\square$ are transmitted herewith (required only if not transmitted by the Inte  | rnational Bureau).   |  |  |  |  |  |
|              |               | b. $\square$ have been transmitted by the International Bureau.  |  |  |  |  |  |  |
|              |               | c. $\square$ have not been made; however, the time limit for making such amend   | lments has NOT expired.  |  |  |  |  |  |
| 775          |               | d. 🖾 have not been made and will not be made.  |  |  |  |  |  |  |
| 9.<br>T0.    |               | A translation of the amendments to the claims under PCT Article 19 (35 U.S.  | C. 371(c)(3)).   |  |  |  |  |  |
| T0.          | $\boxtimes$   | An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).  | i  |  |  |  |  |  |
| ₩1.          |               | A copy of the International Preliminary Examination Report (PCT/IPEA/409)  |  |  |  |  |  |  |
| 12.<br>1     |               | A translation of the annexes to the International Preliminary Examination Rep (35 U.S.C. 371 (c)(5)).  | oort under PCT Article 36  |  |  |  |  |  |
| It           | ems 1.        | 3 to 20 below concern document(s) or information included:   | i  |  |  |  |  |  |
| 13.          | $\boxtimes$   | An Information Disclosure Statement under 37 CFR 1.97 and 1.98.  |  |  |  |  |  |  |
| 14.          |               | An assignment document for recording. A separate cover sheet in compliance   | with 37 CFR 3.28 and 3.31 is included.                                   |  |  |  |  |  |
| 15.          | $\boxtimes$   | A FIRST preliminary amendment.   |  |  |  |  |  |  |
| 16.          |               | A SECOND or SUBSEQUENT preliminary amendment.  |  |  |  |  |  |  |
| 17.          |               | A substitute specification.  |  |  |  |  |  |  |
| 18.          |               | A change of power of attorney and/or address letter.   |  |  |  |  |  |  |
| 19.          | $\boxtimes$   | Certificate of Mailing by Express Mail   |  |  |  |  |  |  |
| 20.          |               | Other items or information:  |  |  |  |  |  |  |
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420 Hecd PCI/PIO \_ 7 JAN 2000

| U.S. APPLICATION NO. (IF KNOWN, SEE 7 CFR INTERNATIONAL APPLICATION NO.  PCT/JP99/02828  |  |                                      |  |                         |          |                    | DOCKET NUMBER -7886US     |                |
|--|--|--------------------------------------|--|-------------------------|----------|--------------------|---------------------------|----------------|
|  | 7 7 7 7                                    |                                      | FC1/31   | 79/0262                 | 40       |                    |                           |                |
| 21. The following BASIC NATIONA  | llowing fees are su                        |                                      | (5)) •   |                         |          |                    | CALCULATION               | S PTO USE ONLY |
| Neither interinterinterinterinterinterinterinter   | rnational prelimin<br>I search fee (37 Cl  | ary examination<br>FR 1.445(a)(2)    | fee (37 CFR 1.482) n                             |                         | \$       | 69 <b>70.0</b> 0   |                           |                |
|  |  |                                      | CFR 1.482) not paid ed by the EPO or JPO         |                         | \$       | 8840.00            |                           |                |
| USPTO but Internation Search Report prepared by the EPO or JPO   |  |                                      |  |                         |          |                    |                           |                |
| ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)  |  |                                      |  |                         |          |                    |                           |                |
| ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)  |  |                                      |  |                         |          |                    |                           |                |
|  |  |                                      | ATE BASIC FE                                     |                         |          |                    | \$970.00                  |                |
| Surcharge of \$130.0 months from the ea  | 00 for furnishing t<br>rliest claimed prio | he oath or decla<br>rity date (37 Cl | ration later than FR 1.492 (e)).                 | □ 20                    | 0 🗆      | 30                 | \$0.00                    |                |
| CLAIMS   | NUMBE                                      | R FILED                              | NUMBER EXT                                       | 'RA                     | RA       |                    |                           |                |
| Total claims   | 7  | - 20 =                               | 0  |                         |          | 8.00               | \$0.00                    |                |
| Independent claims   | •  | - 3 =                                | 0  |                         |          | 8.00               | \$0.00                    |                |
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| must also be filed (   | Note 37 CFR 1.9,                           | 1.27, 1.28) (ch                      | eck if applicable).                              |                         |          |                    | \$0.00                    |                |
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| Processing fee of \$ months from the ea  | 130.00 for furnish rliest claimed prio     | ng the English rity date (37 Cl      | translation later than FR 1.492 (f)).            | □ 20                    | 0 🗆      | 30 +               | \$0.00                    |                |
|  |  |                                      | TOTAL NAT  | IONAI                   | FEE      | =                  | \$970.00                  |                |
| Fee for recording the accompanied by an  | ne enclosed assign<br>appropriate cover    | ment (37 CFR 1<br>sheet (37 CFR      | .21(h)). The assignment 3.28, 3.31) (check if    | ent must b<br>applicabl | e).      |                    | \$0.00                    |                |
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| * .  | nissioner is hereby<br>Account No.         |                                      | harge any fees which r<br>A duplicate copy of th |                         |          |                    | ny overpayment            |                |
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| Lawrence E. Ash  | ery  |                                      |  |                         | SICN     | <u>Cre</u><br>TURE | ul In                     | <i>//</i>      |
| Ratner & Prestia   |  |                                      |  |                         | SIGNA    | TURE               |                           |                |
| P.O. Box 980<br>Valley Forge, PA   | 19482-0980                                 |                                      |  |                         | Lawr     | ence E.            | Ashery                    |                |
| • • •  |  |                                      |  |                         | NAME     | į.                 |                           |                |
|  |  |                                      |  |                         | 34,515   | 5                  | //                        |                |
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PATENT A

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:

T. Hashimoto et al.

: Art Unit:

Serial No.:

09/463,565

: Examiner:

Filed:

Herewith

: Box PCT

FOR:

BATTERY PLATE AND BATTERY

#### SUPPLEMENTAL PRELIMINARY AMENDMENT

Assistant Commissioner for Patents Washington, D.C. 20231

SIR:

Prior to examination, please amend the above-identified application as follows:

#### IN THE CLAIMS:

Please amend claims 1-7 as follows:

- 1 (Amended) An electrode plate for <u>a</u> battery [characterized by using a
- 2 current collector], the electrode plate comprising a [to the] surface [of which]
- 3 having formed thereon an oxide layer, the oxide layer being formed by applying a
- boehmite treatment [is applied, in at least one of the] to the electrode plate surface
- 5 [for positive electrode and electrode plate for negative electrode].
- 1 2. (Amended) [A battery using] The electrode plate as cited in Claim 1
- 2 wherein the electrode plate is included in the [the electrode plate for] battery [as
- 3 cited in Claim 1].

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| 1 | 1 3. (Amended) The electrode plate [1            | for battery] as cited in Claim 1,          |
|---|--|--|
| 2 | wherein the oxide layer has a [the] thickness of | [a thin coating formed on the              |
| 3 | current collector surface by a boehmite treatmen | at ranges from] $0.5 \mu m$ to $5 \mu m$ . |
| 1 | 4. (Amended) The [battery] electroc              | de plate as cited in Claim 2,              |

- 4. (Amended) The [battery] electrode plate as cited in Claim 2,
   wherein the oxide layer has a [the] thickness of [a thin coating formed on the
   current collector surface by a boehmite treatment ranges from] 0.5 μm to 5 μm.
- 5. (Amended) [An] The electrode plate [for battery characterized by using a current collector, to the surface of which a boehmite treatment is applied, in the positive electrode plate] as cited in Claim 1 wherein the electrode plate is selected from the group consisting of a negative electrode plate and a positive electrode plate.
  - 6. (Amended) A [production] method <u>for producing</u> [of] a positive electrode plate for <u>a</u> lithium secondary battery, the method comprising the steps of: <u>providing an electrode plate comprising a metallic foil;</u>

forming a chrome oxide layer on [the surface of a current collector, which is formed of a metallic foil,] the electrode plate by applying a chromate treatment [thereto] to the electrode plate;

applying [a coating of] a paste [containing] <u>comprising</u> an electrode active material to said [current collector] <u>chrome oxide layer</u>; and drying the paste.

7. (Amended) [A lithium secondary battery using a] The method as

cited in Claim 6 wherein the positive electrode plate [that is produced according to

the production method as cited in Claim 6] is included in the lithium secondary

battery.

Please add the following new claims:

1 8. (Newly Added) The electrode plate as cited in Claim 1 further 2 comprising a paste formed on the oxide layer, the paste comprising an electrode 3 active material.

| 1 | 9.              | (Newly Added)       | The electrode plate as cited in Claim 8 wherein the |
|---|-----------------|---------------------|---|
| 2 | paste is a drie | d paste.            |   |
| 1 | 10.             | (Newly Added)       | A method for producing an electrode plate for a     |
| 2 | lithium second  | dary battery, the i | method comprising the steps of:                     |
| 3 | provid          | ing an electrode p  | olate;  |

- forming an oxide layer on the electrode plate by applying a boehmite treatment to the electrode plate;
- applying a paste comprising an electrode active material to the oxide layer;
  and
- 8 drying the paste.

#### **REMARKS**

Claims 1 through 7 have been amended to more clearly point out the inventive features of the present invention. In addition, claims 8-10 have been added. The addition of claims 8-10 is supported by originally filed claim 1, and in the specification at page 2, lines 17-25. No new matter is added.

Respectfully submitted,

RAZNER & PRESTIA

Lawrence E. Ashery, Reg. No. 34,815

Paul D. Golian, Reg. No. 42,591 Attorneys for Applicants

PDG/ap

Dated: April 10, 2000

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(610) 407-0700

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail, with sufficient postage, in an envelope addressed to:
Assistant Commissioner for Patents, Washington, D.C. 20231 on:

**PATENT** 

# 420 Rec'd PCT/PTO 2 7 JAN 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:

T. Hashimoto

: Art Unit: To Be Assigned

Serial No.:

To Be Assigned

: Examiner: To Be Assigned

Filed:

Herewith

FOR:

**BATTERY PLATE AND** 

**BATTERY** 

#### PRELIMINARY AMENDMENT

Assistant Commissioner for Patents Washington, D.C. 20231 S I R:

Prior to examination, please amend the above application as follows:

# IN THE SPECIFICATION:

After the title and before the first paragraph, please insert --THIS APPLICATION IS A U.S. NATIONAL PHASE APPLICATION OF PCT INTERNATIONAL APPLICATION PCT/JP99/02828--.

#### IN THE DRAWINGS:

Please delete page "3/3" of the drawings, also labeled as "Reference Numerals" in its entirety.

Respectfully submitted

Lawrence E. Ashery, Reg. No. 34,515 Attorney for Applicants

LEA/lm

Dated: January 27, 2000

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**EXPRESS MAIL** Mailing Label Number: EL513197405US

Date of Deposit: January 27, 2000

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Kathleen Libby

# 420 Rec'd PCT/PTO Z 7 JAN 2000

#### **SPECIFICATION**

#### BATTERY PLATE AND BATTERY

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#### FIELD OF THE INVENTION

The present invention relates to improvements in electrode plates for battery and a battery using the improved electrode plates for battery.

#### BACKROUND OF THE INVENTION

In order to revent falling of an active material off a current collec-

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tor of a battery due to GUG.
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57261 and H7-13502007

of a chromate treatment or a he current collector has so far amined Publication Nos. S56he manufacturing of electrode

plates for a lithium- ion secondary battery, a method of performing dispersion by kneading under the presence of a surface-active agent is disclosed as the method for improving the wettability of an active material against a bonding agent and a viscosity improver. (The Japanese Patent Unexamined Publication No. H8-190912)

However, it is found difficult for the foregoing electrode plates for battery to achieve an improvement in wettability of an active material against a bonding agent and a viscosity improver and also to satisfy the required adhesiveness between a current collector and an active material after the active material has been applied to the current collector. As a result, after a storage under high temperatures or during repeated charge/discharge operations, the active material peels and falls off the current collector, thereby causing the problem of a reduction in charge/discharge capacity.

The present invention deals with the foregoing unsettled problem to realize a lithium-ion secondary battery which shows minimal corrosion of a current collector due to an active material, minimal peeling and falling of the

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active material off the current collector, thereby demonstrating large discharge capacity.

#### DISCLOSURE OF THE INVENTION

The present invention deals with the afore-mentioned problem to provide an electrode plate for battery and a battery using it, the electrode plate for battery being characterized by applying a boehmite treatment to the surface of a current collector prior to an application of a paste, which is formed of a composition with an active material acting as the principal ingredient, to the current collector.

With a method for producing electrode plates for lithium secondary battery characterized by applying a paste containing a positive electrode active material to a current collector formed of a metallic foil and then drying the paste, the current collector is applied with a chromate treatment on the surface thereof to form a chrome oxide layer prior to the foregoing application of the paste.

The present invention discloses a method for producing electrode plates, the method comprising the steps of:

applying a boehmite treatment to the surface of current collector of one electrode plate selected from a positive electrode plate and a negative electrode plate or applying a chromate treatment to the surface of a positive electrode current collector;

applying a paste formed of a composition containing an electrode active material on the current collector; and

25 drying the paste.

Even when a battery employing the electrodes as described in the above is in usage with repeated charge/discharge operations, a reduction in the charge/discharge capacity and degradation in the load characteristics can be suppressed to a minimum.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a battery in an exemplary embodi-

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ment of the present invention.

Fig. 2 is a diagram to show cycle life characteristics by making a comparison between a prior art battery and a battery in an exemplary embodiment of the present invention.

Fig. 3 is a diagram to show cycle life characteristics by making a comparison between a prior art battery and a battery in another exemplary embodiment of the present invention.

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Next, a description is given to a case where a boehmite treatment is applied to a positive electrode current collector for lithium-ion battery in an exemplary embodiment of the present invention.

### (First Exemplary Embodiment)

A lithium-ion secondary battery in an exemplary embodiment of the present invention is a cylindrical lithium-ion secondary battery as shown in Fig. 1 and formed of a group of electrode plates produced according to the method as disclosed by the present invention, an electrolyte and a battery case 4 accommodating the foregoing. The group of electrode plates includes a sheet like electrode plate 1 for positive electrode, a sheet like electrode plate 2 for negative electrode, a sheet like separator 3 insulating the electrode plate 1 for positive electrode from the electrode plate 2 for negative electrode, a positive electrode lead 7, a negative electrode lead 8, an upper insulating plate 9 and a lower insulating plate 10. The separator 3 is a porous polyethylene film. All of the foregoing elements are superimposed one over another, wound in a spiral fashion and placed inside the cylindrical battery case 4.

The battery case 4 is prepared by applying a deep drawing process to a stainless steel sheet having resistance to an organic electrolyte.

After the group of electrode plates and electrolyte have been placed inside the battery case 4, the opening of the battery case 4 is closed by sealing with a sealing plate 5 and a gasket 6 that acts as an insulator and also applies gas sealing between the sealing plate 5 and the battery case 4.

Now, a description is given to a boehmite treatment.

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After a 30  $\mu$ m thick aluminum foil acting as a positive electrode current collector has been immersed in a 12 cc/l solution of triethanolamine, an oxide film is formed by drying the foregoing aluminum foil for 4 hours at 100 °C to have the surface of the aluminum foil reformed. At this time, the thickness of the oxide film is preferred to be 0.5 to 5.0  $\mu$ m. When the thickness of the oxide film is smaller than 0.5  $\mu$ m, a sufficient effect of reforming the surface of the aluminum foil is not allowed to be realized, resulting in not so excellent adhesion with an active material. On the other hand, when the thickness of the oxide film exceeds 5.0  $\mu$ m, the amount of the active material, which is allowed to be contained in the given same size of the battery case 4, is reduced, resulting in an excessive reduction of the battery capacity to cause an unacceptably large adverse effect.

Next, a description is given to a method for producing the electrode plate 1 for positive electrode. A paste formed of composition with an active material for positive electrode serving as the principal ingredient is prepared by mixing/dispersing 50 weight parts LiCoO<sub>2</sub> powder as the positive electrode active material, 1.5 weight parts acetylene black as a conductive agent, 7 weight parts aqueous solution of 50 weight parts PTFE as a binder and 41.5 weight parts aqueous solution of 1 weight part carboxylmethylcellulose as a viscosity improver. The paste for positive electrode thus prepared is applied to both surfaces of the boehmite treated aluminum foil by using a die coater and, after the coated paste has been dried, the aluminum foil applied with the paste is heated to the melting temperature of PTFE ranging 200 °C to 300 °C, thereby further improving the adhesion between the current collector and the positive electrode composition layer. Then, the aluminum foil is rolled to a thickness of 0.18 mm and cut to produce the sheet like electrode plate 1 for positive electrode of the present invention.

A description is given to a method for producing the electrode plate 2 for negative electrode. A paste for negative electrode is prepared by mixing/dispersing 50 weight parts powder of scale like graphite particles acting as the negative active material, 45 weight parts aqueous solution prepared by dissolving 1 weight part carboxymethylcellulose in 99 weight parts water to

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form a viscosity improver and 5 weight parts styrene-butadiene-rubber as a binder. The paste thus prepared is applied to a 40  $\mu$ m thick copper foil by using a die coater to produce the electrode plate 2 for negative electrode.

The electrolyte is prepared by dissolving LiPF<sub>6</sub> in a mixed solution of 30 vol% ethylene carbonate, 50 vol% diethyl carbonate and 20 vol% methyl propionate to a concentration of 1 mol / 1. This electrolyte is contained inside the battery case, in which the positive electrode active material layer and negative electrode active material layer are impregnated with the electrolyte, thereby causing a cell reaction to take place with the electrolyte serving as a carrier of lithium ions between the electrode plate 1 for positive electrode and the electrode plate 2 for negative electrode by passing through minute holes of the porous separator 3.

A battery is prepared by using the foregoing electrode plate 1 for positive electrode and cycle characteristics of the battery are checked.

The battery thus prepared measures 17 mm in diameter and 50 mm in height.

A battery for comparison, which is the same as the foregoing battery of the present invention except for using a positive electrode current collector with no boehmite treatment applied to the surface thereof, has been prepared to carry out a side-by-side performance evaluation.

The battery of the present invention and the battery for comparison are subjected to a cycle test, one cycle of which comprises the steps of constant current charging at 500 mA until the battery voltage reaches 4.1 V, switching to constant voltage charging when the battery voltage reaches 4.1 V, continuing the constant voltage charging until the total charging time reaches 2 hours, starting discharging at 720 mA in an ambient temperature of 20 °C and suspending the discharging when the discharge voltage decreases to 3.0 V. Upon completing one cycle as above, the next cycle is started. Fig. 2 shows the results of the cycle test, i.e., cycle life characteristics, on the foregoing battery of the present invention and the battery for comparison with a capacity maintenance ratio indicated on the vertical axis and a number of cycles on the horizontal axis when charge/discharge operations as described in the above are repeated. It is found out from Fig. 2 that the battery of the present in-

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vention shows little degradation in capacity after repeated charge/discharge operations when compared with the battery for comparison, thereby proving that the battery of the present invention has excellent cycle characteristics.

This is because of the needle like structure formed on the surface of the positive electrode current collector by an application of a boehmite treatment thereto and the enhanced adhesion between the current collector and the composition layer with the active material acting as the principal ingredient, the enhanced adhesion having been realized by the polymeric material of PTFE entangled with the needle like structure in a three-dimensional manner to demonstrate an anchor effect. Therefore, even when the composition layer containing the active material expands/shrinks due to repeated charge/discharge operations, it is hard for the composition layer to get separated from the current collector.

Also, the battery of the present invention and battery for comparison are kept in storage under a charged condition for 20 days at 60 °C and then subjected to several times of repeated charge/discharge operations at room temperature, followed with a discharging operation at 720 mA to find capacity till the time when the battery voltage reaches 3.0 V. The resulting capacity is compared with the capacity just before being kept in storage and Table 1 shows the findings.

Table 1

| High Temperature Storage  | Battery of Present | Battery for |
|---|--------------------|-------------|
| Characteristics   | Invention          | Comparison  |
| (Capacity after Storage/<br>Capacity before Storage) ×<br>100 (%) | 98                 | 93          |

As shown in Table 1, the battery of the present invention is found to show little degradation in capacity even under a high temperature storage condition.

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A case, where the boehmite treatment is applied to the positive electrode current collector for a lithium secondary battery, is shown in the present exemplary embodiment but the boehmite treatment is also allowed to be applied to the negative electrode current collector for the same effect, and further the same effect can be gained even when the boehmite treatment is applied to electrode plates of other battery systems.

#### (Second Exemplary Embodiment)

The preparation of an electrode plate 1 for positive electrode is made in the same way as in the first exemplary embodiment except for using an aluminum foil, on the surface of which a chromium oxide layer is formed in advance by a chromate treatment, in place of an aluminum foil that is boehmite treated.

A paste for negative electrode used with an electrode plate 2 for negative electrode is prepared according to the same method as employed in the first exemplary embodiment. The obtained paste for negative electrode is applied to both surfaces of a negative electrode current collector formed of a 50 µm thick copper foil by using a die coater and the applied paste is dried. Then, the copper foil is rolled to a thickness of 0.2 mm and cut to produce a sheet like electrode plate 2 for negative electrode.

An electrolyte, which is the same one as used in the first exemplary embodiment, is used in the present exemplary embodiment.

A battery is produced by using the foregoing electrode plate 1 for positive electrode in the same way as the first exemplary embodiment and the cycle characteristics of the battery are checked. The battery thus produced measures 17 mm in diameter and 50 mm in height.

As a battery for comparison is used a lithium secondary battery prepared according to the same method as employed in the first exemplary embodiment except for using a positive electrode current collector without applying any chromate treatment to the surface thereof. Then, a comparison is made between the battery for comparison of above and a lithium secondary battery using the positive electrode plate prepared according to the method of the present invention and the cycle characteristics of both batteries are as

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shown in Fig. 3.

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In the same way as in the first exemplary embodiment, the batteries are charged with a constant current of 500 mA and then, when the battery voltage has reached 4.1 V, charging of the batteries is switched to constant voltage charging, the constant voltage being 4.1 V, with the total charging time extended to as long as 2 hours. Discharging of the batteries is performed with a discharge current value of 720 mA at 20 °C and, when the dicharge voltage has reached 3.0 V, the discharge cycle is ended and a new charge cycle is started. What is found out from Fig. 3 is that the lithium secondary battery using the electrode plate for positive electrode produced according to the method of the present invention shows little degradation in capacity in comparison with a lithium secondary battery using the electrode plate for positive electrode prepared according to the conventional method even when a charge/discharge operation is repeated, thus demonstrating excellent cycle characteristics.

This is because of the following reason. The battery using the electrode plate for positive electrode of a lithium secondary battery prepared according to the production method of the present invention shows a reduction in corrosion of the current collector caused by a composition layer since the composition layer with the principal ingredient thereof formed of an active material does not come into a direct contact with the current collector although the surface of the positive electrode current collector is chromate treated and the chromate treated coating on the surface of the current collector is corroded, and further since generation of hydrogen gas, which takes place in the vicinity of an interface between the two different substances at the time of corrosive reaction, can be suppressed, the adhesion between the positive electrode composition layer and the current collector is enhanced, thereby making it hard for the positive electrode composition layer to peel off from the current collector even if the positive electrode composition layer undergoes expansion/shrinkage due to charge/discharge operations of the battery.

In addition, when an aluminum foil is used to form the positive electrode current collector, the surface of the aluminum foil is corroded moderately by the chromate treatment applied thereto, thereby enhancing markedly the adhesion of the positive electrode composition layer to the current collector because of the anchor effect created on the surface of the aluminum foil. On the other hand, when an iron foil is used to form the current collector, the anchor effect due to the chromate treatment is small.

Lithium secondary batteries prepared by the use of these electrode plates for positive electrode are kept in storage under a charged condition for 20 days at 60 °C, and then subjected to several times of repeated charge/discharge operations at room temperature, followed with a discharging operation at 720 mA to find capacity till the time when the battery voltage reaches 3.0 V. The resulting capacity is compared with the capacity just before being kept in storage and Table 2 shows the findings.

Table 2

| High Temperature Storage  | Battery of Present | Battery for |
|---|--------------------|-------------|
| Characteristics   | Invention          | Comparison  |
| (Capacity after Storage/<br>Capacity before Storage) ×<br>100 (%) | 99                 | 93          |

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As shown in Table 2, a lithium secondary battery using an electrode plate for positive electrode prepared according to the production method of the present invention is found to show little degradation in capacity even under a high temperature storage condition.

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#### INDUSTRIAL USABILITY

As described in the above, the present invention makes it possible for a secondary battery to suppress the degradation in charge/discharge capacity and storage characteristics to an extremely small extent when the battery is used in repeated charge/discharge operations.

In addition, even under such a stringent condition as the battery is in storage at high temperatures for a long period, the degradation in charge/discharge capacity can be suppressed to a minimum. Also, a composition layer formed of an active material acting as the principal ingredient thereof is prevented from peeling off the current collector of an electrode plate during the assembly work of batteries, thereby enabling the enhancement of workability involved with the assembly work of the batteries.

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#### **CLAIM**

- An electrode plate for battery characterized by using a current collector, to the surface of which a boehmite treatment is applied, in at least one of the electrode plate for positive electrode and electrode plate for negative electrode.
- 2. A battery using the electrode plate for battery as cited in Claim 1.
- 3. The electrode plate for battery as cited in Claim 1, wherein the thickness of a thin coating formed on the current collector surface by a boehmite treatment ranges from  $0.5~\mu m$  to  $5~\mu m$ .
- 4. The battery as cited in Claim 2, wherein the thickness of a thin coating formed on the current collector surface by a boehmite treatment ranges from 0.5 μm to 5 μm.
  - 5. An electrode plate for battery characterized by using a current collector, to the surface of which a boehmite treatment is applied, in the positive electrode plate.
  - 6. A production method of a positive electrode plate for lithium secondary battery, the method comprising the steps of:
    forming a chrome oxide layer on the surface of a current collector, which is formed of a metallic foil, by applying a chromate treatment thereto; applying a coating of a paste containing an electrode active material to said current collector; and drying the paste.
  - 7. A lithium secondary battery using a positive electrode plate that is produced according to the production method as cited in Claim 6.

#### **ABSTRAT**

What is made available by the present invention is a battery, in which measures are taken to suppress a reduction in charge/discharge capacity and degradation of load characteristics due to peeling of an active material off the current collector during the use of the battery with charge/discharge operations repeated. An application of a boehmite treatment or a chromate treatment to the current collector surface of the electrode plate for the battery makes it possible for the degradation of charge/discharge capacity and load characteristics to be suppressed to a minimum.

Fig 1

# 1/3

| 1.  | Electrode Plate for Positive Electrode |
|-----|--|
| 2.  | Electrode Plate for Negative Electrode |
| 3.  | Separator                              |
| 4.  | Battery Case                           |
| 5.  | Sealing Plate                          |
| 6.  | Gasket                                 |
| 7.  | Positive Electrode Lead                |
| 8.  | Negative Electrode Lead                |
| 9.  | Upper Insulating Plate                 |
| 10. | Lower Insulating Plate                 |

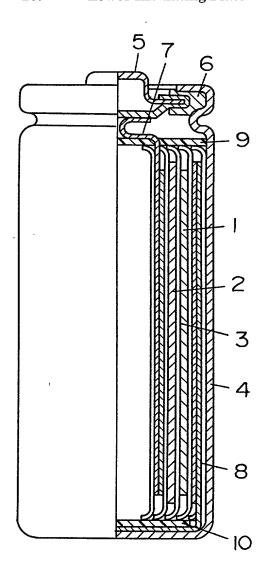


Fig 2

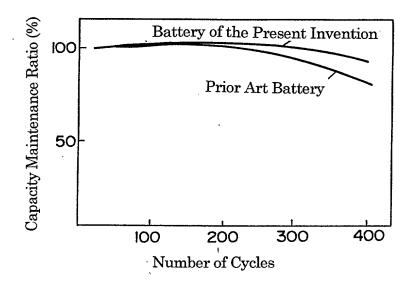
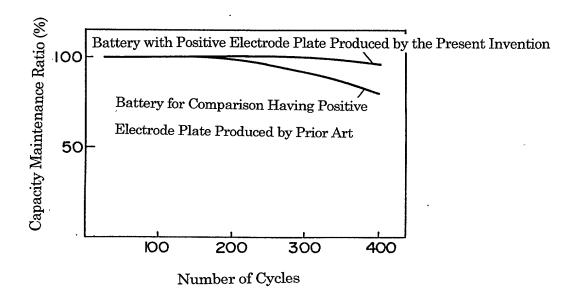


Fig 3



# 3/3

# Key to Reference Numerals

| 1.  | Electrode Plate for Positive Electrode |
|-----|--|
| 2.  | Electrode Plate for Negative Electrode |
| 3.  | Separator                              |
| 4.  | Battery Case                           |
| 5.  | Sealing Plate                          |
| 6.  | Gasket                                 |
| 7.  | Positive Electrode Lead                |
| 8.  | Negative Electrode Lead                |
| 9.  | Upper Insulating Plate                 |
| 10. | Lower Insulating Plate                 |

R:372

|   | Declaration a  | nd Po      | ower o       | f Attor      | ney For<br>Declaration | Patent A       | App    | alic                    | aţ     | lon    |
|---|--|------------|--------------|--------------|------------------------|----------------|--------|-------------------------|--------|--------|
|   | As a below named inventor, I hereby declare that:  My residence, post office address and citizenship are as stated below next to my name (TRADENNAME)  |            |              |              |                        |                |        |                         |        |        |
|   | My residence, post offi  | ce addres  | s and citize | enship are a | s stated below         | v next to my r | name   | Ye ro                   | 4 NES  | ARHER  |
|   | I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled <a href="BATTERY PLATE AND BATTERY">BATTERY</a> . The specification of which is attached hereto unless the following box is checked:  was filed on <a href="May 27, 1999">May 27, 1999</a> as  United States Application Number or PCT International Application Number <a href="PCT/JP99/02828">PCT/JP99/02828</a> and was amended on <a href="January 27, 2000 (by preliminary amendment">January 27, 2000 (by preliminary amendment</a> ) (if applicable).  I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. |            |              |              |                        |                |        |                         |        |        |
|   | I acknowledge the duty   | to disclo  | se informati | ion which is | material to pa         | tentability as | defin  | ed in :                 | 37 C   | FR§    |
| W.  | I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed: Prior Foreign Application(s)   |            |              |              |                        |                |        |                         |        |        |
|   |  | Japan      |              |              | 28 May 1998            |                |        | 1                       | $\Box$ |        |
| Hand Hand   | (Harriber)   | (Country)  |              |              | (Day/Month/Year        | Filed)         |        |                         |        |        |
|   | (Number)   | (Country)  |              |              | (Day/Month/Year        | ·<br>· Filed)  |        |                         |        |        |
| P. Ree Will Last  | hereby claim the bend<br>below.  | efit under | 35 U.S.C. §  | 119(e) of a  | ny United State        | es provisiona  | i appi | icatio                  | n(s)   | listed |
| (Application Number) (Filing Date)  |  |            |              |              |                        |                |        |                         |        |        |
| -   | •  | -          |              |              |                        |                |        |                         |        |        |
|   | (Application Number)   |            | •            |              |                        |                |        |                         |        |        |
| I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of PCT International application designating the United States, listed below and, insofar as the submatter of each of the claims of this application is not disclosed in the prior United States or International application in the manner provided by the first paragraph of 35 U.S.C. § 11 acknowledge the duty to disclose information which is material to patentability as defined in 37 CF |  |            |              |              |                        |                |        | ubject<br>PCT<br>112, 1 |        |        |

acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

| (700年04月20日(末) 1                      | 7時41分離: 51-                      | ura :  | 発信:松下技術情報サービス(株                    |   | R: 372                            | P. 0 |
|---------------------------------------|----------------------------------|--|------------------------------------|---|-----------------------------------|------|
|                                       | IIIM 5 8 5000 R                  |  |                                    |   |                                   |      |
| (Application Number                   | Jun 1                            | (Filing Date)                                  | (Status - pater                    | nted, pending, abando                       | ned)                              |      |
| (Application Number                   | TRADEMAR!                        | (Filing Date)                                  | (Status - pater                    | nted, pending, abando                       | ned)                              |      |
|                                       |                                  | named inventor,                                |                                    |   |                                   |      |
| connected there                       |                                  | cation and transact                            | all business in                    | me Patent and Th                            | agemark On                        | ice  |
| Paul F. Prestia<br>Allan Ratner       | Reg.No. 23,031<br>Reg.No. 19,717 | Lawrence E. Ashery<br>Robert L. Andersen       | Reg.No. 34,515<br>Reg.No.25,771    | Mark J. Marceili<br>Joshua L. Cohen         | Reg.No. 36,59                     | 40   |
| Andrew L. Ney<br>Kenneth N. Nigon     | Reg.No. 20,300<br>Reg.No. 31,549 | Christopher R. Lewis<br>Louis W. Beardell, Jr. | Reg.No. 36,201<br>Reg.No. 40,506   | Christopher J. Dervisi<br>Jack J. Jankovitz | nian Reg.No. 42,4<br>Reg.No. 42,6 |      |
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| Benjamin E. Leace<br>James C. Simmons | Reg.No. 33,412<br>Reg.No. 24,842 | Jacques L. Etkowicz<br>Eric A. Dichter         | Reg.No. P41,738<br>Reg.No. P41,708 | -   | 18                                |      |
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| wiltui taise state                    | ements may jeop                  | pardize the validity of                        | or the application                 | or any patent issu                          | jea thereon.                      |      |
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|                                       |                                  |  |                                    |   |                                   |      |
| Additional inv                        | ventors are being nar            | ned on separately numb                         | ered sheets attached               | hereto.                                     |                                   |      |

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